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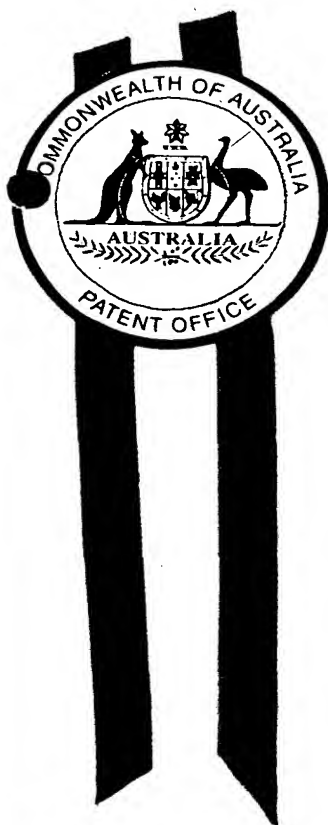
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I, LEANNE MYNOTT, ACTING MANAGER PATENT ADMINISTRATION
hereby certify that annexed is a true copy of the Provisional specification in
connection with Application No. PQ 1642 for a patent by ORICA AUSTRALIA
PTY LIMITED filed on 14 July 1999.

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LEANNE MYNOTT
ACTING MANAGER PATENT
ADMINISTRATION



Orica Australia Pty Limited

A U S T R A L I A
Patents Act 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"Aqueous Polymer Dispersion"

The invention is described in the following statement:

- 1A -

AQUEOUS POLYMER DISPERSION

This invention relates to the production and use of aqueous dispersions of water insoluble heteropolymeric particles. In particular it relates to the incorporation of reactive amphiphilic moieties into such polymeric particles to provide aqueous dispersions exhibiting a temperature
5 dependent viscosity. The invention also relates to the use of these aqueous dispersions as binders or thickeners for paints, adhesives, textile coatings, carpet backings and construction materials. The aqueous dispersions are particularly useful in the preparation of paints and accordingly it will be convenient to hereinafter describe the invention with reference to this application, however it is to be understood that the aqueous dispersions have other
10 applications.

U.S. Patent No. 4,468,498 (Kowalski) describes a sequential emulsion polymerisation process for making an aqueous dispersion of water insoluble heteropolymeric particles having a core/sheath (or shell) structure. The core, which contains acid monomers, is alkali
15 swellable such that addition of base to the polymerised particles to neutralise the acid monomers results in hydration of the core and swelling of the particles. The swelling allows the aqueous dispersion to be used as a thickener for water based coating compositions. It is also suggested that the dispersion could be used as a binder or part thereof in a water based coating composition.

20

It has now been found that the incorporation of a reactive amphiphile into a water insoluble heteropolymer during polymerisation and under particular conditions can enhance the thickening of an aqueous dispersion of the heteropolymer and provide an aqueous dispersion exhibiting a temperature dependent viscosity.

25

Accordingly in a first aspect the present invention provides a process for preparing an aqueous dispersion of water insoluble polymer particles comprising:

- a) preparing by polymerisation an aqueous dispersion of water insoluble particles of a
30 heteropolymer including monomeric units of a reactive amphiphile having a cloud point and monomeric units of a hydrophilic monomer, said polymerisation being

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conducted in the presence of a stabilising agent and the reactive amphiphile and at a temperature above the cloud point of said amphiphile,

- b) cooling said aqueous dispersion to a temperature below the cloud point of the reactive
5 amphiphile such that the viscosity of the aqueous dispersion increases.

As used herein the term "cloud point" refers to the temperature at which the molecules of reactive amphiphile disassociate from the water molecules with which they are hydrated to the extent that they form a separate phase. In the absence of monomers this event results in a
10 separation of an aqueous solution of the amphiphile into two phases, one being a phase rich in surfactant and the other being an aqueous equilibrium mixture in which relatively little surfactant is present. This phase separation causes a clear solution of the amphiphile to become cloudy, and hence the term "cloud point". In the emulsion polymerisation process of the present invention it is believed that this event results in the amphiphile becoming
15 associated with and embedded in the oil phase of the emulsion.

Many factors effect the cloud point of an amphiphile. Several of these factors are described in Chapter 11 of Nonionic Surfactants Chemical Analysis Vol. 19 Surfactant Science Series John Cross published by Marcel Dekker, Inc. 1987 which is incorporated herein by
20 reference.

While the exact temperature at which the amphiphile dissociates from its water of hydration in the emulsion polymerisation medium is difficult to measure, it can be approximated by measuring the cloud point of the amphiphile in an aqueous composition similar to the aqueous
25 phase of the emulsion. As indicated in Chapter 11 of the reference above it is possible to lower the cloud point of an amphiphile by changing the composition of the aqueous phase. For example it is possible to change the cloud point of an amphiphile by addition of electrolytes, such as those based on alkali metal ions. Addition of such electrolytes generally causes a depression of the cloud point which can be quite marked.

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The term "cloud point" is normally only applicable to nonionic amphiphiles, however some ionic surfactants also have a cloud point at a pH at which the surfactants are uncharged. For example anionic surfactants, such as phosphates or carboxylates, may have a cloud point below the pKa of the phosphate or carboxylate. Similarly cationic surfactants, such as amine 5 surfactants, may have a cloud point above the pKb of the amine group.

The reactive amphiphile may be any amphiphilic compound having a cloud point and being capable of being incorporated into the heteropolymer. The amphiphile may be incorporated into the "backbone" of the heteropolymer or the amphiphile may become incorporated into 10 the heteropolymer by reacting with functional groups present on the "backbone" monomers.

Examples of reactive amphiphiles capable of being incorporated into the backbone of the heteropolymer include surfactants having one or more polymerisable double or triple bonds, such as the unsaturated fatty acid and fatty alcohol alkoxylates. Examples of such reactive 15 amphiphiles include undecylenic acid ethoxylate, undecylenol ethoxylate, linoleyl acid ethoxylate, linoleyl alcohol ethoxylate and octenol ethoxylate. The reactive amphiphile may include block copolymers of propoxylate, ethoxylate and/or butoxylate with a reactive group or may be an ethoxylated alcohol or acid with propylate or butoxylate attached.

20 Examples of reactive amphiphiles capable of reacting with a functional group of a backbone monomer include those unsaturated amphiphiles described above, as well as amphiphiles having terminal or pendant reactive groups, such as carboxylates, sulphates, sulphonates, phosphates, primary or secondary amino and other groups known to those skilled in the art as being capable of reacting with the backbone monomers (whether before or after 25 incorporation into the heteropolymer) under the polymerisation conditions employed. The amphiphile used in a particular polymerisation will depend on the nature of the functional groups present on the backbone monomers.

Examples of reactive amphiphiles capable of reacting with a functional group of a 30 backbone monomer include phosphates, such as stearyl ethoxylate phosphate or carboxylates, such as alkylsuccinic anhydride ethoxylate, and polyether amines, such as

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Jeffamine M2070. Any of these surfactants may be employed provided the polymerisation medium is such that the amphiphile has a cloud point.

Examples of backbone monomers which include functional groups capable of reacting with
5 such reactive amphiphiles include glycidyl methacrylate or acrylate, acetyl
acetoethylmethacrylate, or isocyanate containing monomers such as 2-isocyanatoethyl
methacrylate. A person skilled in the art would be able to readily determine combinations
of reactive groups on amphiphiles and reactive groups on backbone monomers which
would allow incorporation of the reactive amphiphile into the heteropolymer.

10

The reactive group of the amphiphile may be present in either the hydrophobic or the
hydrophilic region of the amphiphile.

The exact nature of the amphiphile employed will depend on several factors, the most
15 important of which is the cloud point. Accordingly the degree of alkoxylation, width of
distribution of alkoxylation numbers etc. of a given type of amphiphile is governed by the
cloud point of the resulting amphiphile in the polymerisation medium employed.

Preferably the amphiphile has a cloud point of at least 10°C above the normal use
20 temperature of the water-based composition or paint. Accordingly the amphiphile
preferably has a cloud point of greater than 45°, more preferably above 50° and most
preferably between 50° and 100°C.

The amount of amphiphile employed will also depend on several factors, including the
25 desired end use of the dispersion, however the amount of amphiphile will preferably be
from 1-35%, more preferably 3 to 15% by weight of the heteropolymer.

The term "hydrophilic monomers" as used herein refers to monomers which have a
solubility in water of at least 5g/L. Examples of suitable hydrophilic monomers include
30 methyl methacrylate, ethyl acrylate, vinyl acetate, methyl acrylate, acrylic acid,
methacrylic acid, propyl acrylate, isopropyl methacrylate, hydroxy ethyl methacrylate,

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hydroxy propyl methacrylate, acrylamide and methacrylamide. Other examples of water soluble monomers would be known to those skilled in the art. The hydrophilic monomers preferably make up 5% to 99%, more preferably 60 to 95% by weight of the heteropolymer.

5

In a preferred embodiment at least a portion of the hydrophilic monomers have ionizable groups. The ionizable groups may be acid groups or basic groups. Examples of suitable acid monomers include methacrylic acid, acrylic acid, itaconic acid, p-styrene carboxylic acids, p-styrene sulfonic acids, vinyl sulfonic acid, vinyl phosphonic acid, ethacrylic acid, 10 alpha-chloroacrylic acid, crotonic acid, fumaric acid, citraconic acid, mesaconic acid and maleic acid. Examples of readily available basic monomers include 2-(dimethyl amino) ethyl and propyl acrylates and methacrylates, and the corresponding 3-(diethylamino) ethyl and propyl acrylates and methacrylates. Alternatively, the required basic groups could be formed *in situ* by post reaction of such functional monomers such as glycidyl methacrylate 15 with a suitable amine co-reactant, typically a secondary amine. Preferably the ionizable monomers make up 0.1 to 40%, more preferably between 1 and 20% and most preferably 1 to 10% by weight of the heteropolymer.

In addition to the hydrophilic monomers the heteropolymer may contain some monomers 20 having a water solubility less than 5g/L. The presence of hydrophobic monomers may reduce the ability of the particles to swell. It may be possible to compensate for this effect of the hydrophobic monomers, for example, by increasing the proportion of ionizable monomers or hydrophilic groups. The presence of hydrophobic monomers can contribute to the film properties of a resultant coating. Examples of less soluble monomers which 25 may be incorporated into the heteropolymer include styrene, alpha-methyl styrene, butyl acrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, lauryl methacrylate, stearyl methacrylate, ethyl hexyl methacrylate, crotyl methacrylate, cinnamyl methacrylate, oleyl methacrylate, ricinoleyl methacrylate, vinyl butyrate, vinyl tert-butylate, vinyl stearate, vinyl laurate etc. Preferably these less soluble monomers make 30 up less than 75% by weight, more preferably less than 45% and most preferably less than 10% of the heteropolymer.

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The monomers may be utilised in monomeric form or in the form of prepolymers. For example the acid monomers may be added in prepolymerised form, either in the form of a pre-homopolymer or as a pre-copolymer with one or more of the hydrophilic monomers.

- 5 The monomer composition may further include monomers with more than one reactive group as crosslinking agents. Examples of suitable polyfunctional monomers include glycerol propoxy triacrylate, glycerol propoxy trimethacrylate, trimethylolpropane triacrylate and trimethylolpropane trimethacrylate. The crosslinking agent may be added in an amount of 0 to 10%, more preferably 0.001 to 4% by weight of the heteropolymer.
- 10 Care should be taken with the inclusion of crosslinking agents as their presence can lead to difficulties in controlling the particle size and elimination of coagulation.

Alternative methods of providing controlled crosslinking may be incorporating an appropriate concentration of functional monomers typically used by persons skilled in the

15 art. Such monomers include, 2-isocyanatoethyl methacrylate, N-methyl acrylamide, and glycidyl methacrylate or acrylate. Such functional monomers would be designed to react completely with an appropriate complementary coreacting functional monomer such as acid monomer, hydroxy monomer, or combinations. A wide range of crosslinking reactions are possible.

20

While not wishing to be limited by theory it is believed that conducting the polymerisation at a temperature above the cloud point allows the reactive amphiphile to become embedded in the particles at a temperature above its cloud point. It is also believed that ionizable monomers can play a role in embedding the amphiphile in the particles by associating with

25 the hydrophilic portion of the amphiphile, such as with the polyoxyalkylene segments present in alkoxyated surfactants. As the particles cool it is believed that the amphiphile becomes more hydrated, thereby resulting in thickening of the dispersion. This thickening is greatly enhanced by addition of a suitable neutralising agent which neutralises the ionizable monomer units causing further swelling of the particles.

30

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A common requirement within the typical formulating practices for waterborne latex based products is that they rely on the use of rheological additives and other modifiers to a much greater extent than their solvent based counterparts. Depending on the end use, a typical latex paint might contain four or five different additives to provide the balance of
5 viscosities required for application, anti-settling and flow characteristics and to optimise film formation.

Conventional waterborne coatings typically rely on the inclusion of some co-solvent as an aid to film formation and giving the particles sufficient deformability to bind the pigment
10 particles and hence form useful films. The added co-solvent evaporates from the film both during and after film formation contributing to unwanted odour and environmental damage.

Within the group of rheological control additives, one class are the so called alkali
15 swellable acrylic thickeners (ASA), which are acid containing acrylic latex copolymers. When neutralised with ammonia, such materials become thick, viscous liquids. These materials rely on relatively high levels of acid monomers to achieve their thickening effects and are sensitive to other formulation ingredients. Thickening function can be reduced in the presence of co-solvent hence requiring increased levels for the required
20 performance. Under some conditions, the presence of high levels of acid monomer will contribute to increased water sensitivity of the final film which makes them impractical as sole vehicles for use in most applications.

Other classes of rheological control additives other than alkali swellable acrylics are
25 available which are used in combination with ASA types depending on the application and rheological profile required.

This invention provides a formulating approach which is capable of overcoming both of these limitations. A latex can be formulated which can be used as a sole binder in a paint
30 film without the use of co-solvent or external rheological control additives of any sort. For this objective it is preferable to carry out a sequential polymerisation where the reactive

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amphiphile and acidic monomer are concentrated in a single first feed, or "core" feed. The second feed of monomer is termed the "shell" feed.

A binder with high swelling ratio may be one where the core feed composition is a
5 substantial portion of the total polymer. Such a problem is presented by the formulation of a sealer/binder paint with low volatile organic content (VOC). The level of reactive amphiphile and acidic monomer may be chosen so as to achieve the required swelling ratio in the final latex and paint. An alternative formulating approach would be to concentrate the reactive amphiphile/acidic monomer combination so that the core composition will
10 swell to a greater extent at lower core levels. Such a composition may be formed by using higher levels of acid monomer with a given level of reactive amphiphile.

The glass transition temperature (T_g) is related to the hardness of a polymer, and is related to the proportion of hard and soft monomers. In conventional latex formulations the T_g of
15 the polymer will be designed to have a direct relationship to the conditions of use by balancing hard monomer such as methyl methacrylate against a soft monomer such as ethyl acrylate. Thus in general, latices will be formulated to have a T_g not exceeding 30°C . For coatings applications, considerably lower T_g latices may be formulated where the T_g may be as low as 0°C or lower.

20 For the dispersions which are the subject of this invention, the presence of the reactive amphiphile will act to reduce the T_g of the core material. Plasticisation of the core will occur once it is neutralised and swells. Hence the hardness of the core material is not a controlling factor in film formation and dispersions with T_g considerably above that of
25 conventional film forming latices are possible. Where the T_g of the core material is very hard typically above 45°C , the process of neutralisation and swelling is best carried out at reaction temperature.

The combination of reactive amphiphile/acidic monomer is exclusively in this core feed.
30 Concentration of the core amphiphile in this way is particularly favourable allowing extensive swelling behaviour at low acid levels. The combination of amphiphile and acidic

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monomer is important to achieving the maximum swelling effect for given core/shell ratio. Where the latex application is to achieve maximum particle swelling and the resulting composition is to be used as an additive thickener latex, the level of acid monomer may be higher. In these cases, it may also be preferable to construct the latex using a single
5 non-sequential feed of uniform composition.

In cases where the Tg of the shell is low the formulation of the second monomer feed (the shell) is also determined by the final application. The composition may not be film forming at ambient temperature (MFFT above about 23°C) until the latex is neutralised
10 and the particle swells becoming plasticised by water. In this condition the MFFT can drop considerably without the addition of other coalescing aids. With the use of more hydrophobic monomers, such as butyl acrylate, is possible to produce swollen latex particles with more associative effects. Under some conditions latices which show controlled shear thickening are possible.

15

Particle swelling during neutralisation can be carried out at any temperature including ambient temperature. Under these conditions limitation of the overall Tg of the particle particularly the shell are favoured. However, swelling of very hard particles is possible and may involve the addition of the neutralising base at reaction temperatures. This may
20 limit the polymer concentration or solids content of the dispersion which can be prepared such that the dispersion will remain pourable or pumpable during use.

The polymerisation is conducted in aqueous solution and may be performed using micro, mini or conventional emulsion polymerisation, suspension or dispersion polymerisation.
25 Preferably the polymerisation is an emulsion polymerisation.

To obtain particles having the required properties the polymerisation must be performed in the presence of a stabilising agent. The type of stabilising agent will depend on the monomer composition used, type of polymerisation, temperature of the polymerisation,
30 nature of the reactive amphiphile etc. Preferred stabilising agents include anionic surfactants, such as sodium dodecyl sulfate, nonyl phenol ethoxylate sulfate, alkyl

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ethoxylate sulfates, alkyl sulfonates, alkyl succinates, alkyl phosphates, alkyl carboxylates, and other alternatives well known to those skilled in the art. Other stabilising agents include polymeric stabilisers, cationic surfactants or non-ionic surfactants with cloud points above the polymerisation temperature.

5

The particle size of the polymer emulsion is related to the level of stabilizing agent used during the polymerisation. In order to obtain the optimum swelling of the particles, the stabilizer must be present in the correct amount to induce encapsulation of the reactive amphiphile and other hydrophilic material by the polymer, and not to result, for instance
10 in nucleation of new particles late in the polymerisation process.

The polymerisation process requires an initiating mechanism. The type and nature of the initiator or initiator system will depend on the types of monomers and the nature of the polymerisation.

15

For example, the polymerisation can be initiated by water soluble initiators such as ammonium persulfate, potassium persulfate, tertiary butyl hydroperoxide and sodium sulfite formaldehyde, or oil soluble initiators such as tertiary butyl perbenzoate or azo initiating compounds, such as AIBN. These can be used as thermal initiators or in suitable
20 redox pairs well known to those skilled in the preparation of aqueous dispersions.

The emulsion polymerisation should be conducted at a temperature above the cloud point of the reactive amphiphile. Preferably the polymerisation temperature is more than 5°C above the cloud point, more preferably more than 10°C. The reaction is preferably
25 conducted at a temperature below 120°C, more preferably below 100°C.

As mentioned above the thickening which occurs as a result of cooling the heteropolymer dispersion from the reaction temperature to below the cloud point of the reactive amphiphile can be enhanced by neutralisation of at least a portion of the ionizable groups
30 of any ionizable monomer units. This can be achieved by adding a suitable neutralizing agent following polymerisation, or it can be achieved by adding the dispersion to an

aqueous composition which is already alkaline or acidic or to which a base or acid is subsequently added. Examples of bases which may be used to neutralise the acid groups include alkali metal bases, such as NaOH, KOH, Na_2CO_3 and NaHCO_3 , ammonium hydroxide, alkaline earth metal bases such as $\text{Ca}(\text{OH})_2$, or lower aliphatic amines, such as
5 trimethylamine and triethylamine. Examples of acids which may be used to neutralise the basic groups include mineral acids, such as HCl, H_2SO_4 , HNO_3 and H_3PO_4 and organic acids, such as acetic acid, lactic acid, formic acid, citric acid and oxalic acid.

The dispersions of the present invention exhibit a temperature dependent viscosity, even
10 after neutralisation. After polymerisation the dispersion is cooled to below the cloud point of the reactive amphiphile resulting in a swelling of the particles. Raising the temperature again can result in a reduction in viscosity (i.e. thinning), although this need not give the same viscosity as the original viscosity at that temperature. On reheating a dispersion which has been neutralised, the non-ionic component becomes dehydrated and the particles
15 tend to shrink in volume. The viscosity in this case will generally not return to its original pre-neutralised value because of the presence of the neutralised ionizable groups, although the viscosity may be indistinguishable from the original high temperature viscosity.

As used herein the term "core" refers to the internal region of the polymeric particles and
20 the term "sheath" refers to the outer regions. Throughout the specification the polymeric particles can often be referred by references to this core/sheath type structure. While the core/sheath terminology implies that the particles are composed of two separate structural components, of possibly different composition, it is to be understood that the particles may not have this exact structure and that the distinction between the core and the sheath may
25 not be as precise as suggested by this terminology.

The aqueous dispersion of the present invention may be prepared via a single polymerisation step or the polymerisation may be conducted sequentially. Since it is the core which must contain the ionizable groups and the reactive amphiphile, when
30 conducting the polymerisation sequentially it may not be necessary to include ionizable monomers or reactive amphiphiles in the outer layers or sheath. It has been found

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however that the presence of some ionizable monomers in the outer layers can assist penetration of the neutralising base and water into the core region. The presence of other hydrophilic monomers, such as those containing hydroxy, amide or ureido groups, may also assist in penetration of the neutralising agent. Conducting the polymerisation
5 sequentially has several advantages, one of which is that the particles can be prepared in which the core and sheath have different compositions. When conducting the polymerisation sequentially it is important that the outer layers or sheath are permeable to the neutralising agent and water. It is also important that when the dispersion is to be used as a paint binder that the sheath has a composition which allows coalescence and film
10 formation on curing of the paint. The coalescence and film formation may be aided by swelling of the particles with water, and the minimum film forming temperature (MFFT) may be considerably lower than the polymer glass transition temperature (T_g). The actual MFFT of a particular latex will change with the extent of neutralisation of the internal acid groups and the extent of water uptake and thickening. If necessary a conventional solvent
15 such as Texanol™ (from Eastman) or Coasol™ (from Chemoxy Int.) may be added to assist coalescence and film formation.

The particles having the core and sheath structure described above are a particularly preferred embodiment of the present invention.

20

Accordingly in a further aspect the invention provides an aqueous dispersion of water insoluble heteropolymer particles wherein said heteropolymer particles comprise a polymeric core incorporating units of a reactive amphiphile having a cloud point, units of reactive amphiphile being substantially hydrated, and a sheath comprising at least a portion
25 of polymerised hydrophilic monomers, said dispersion exhibiting temperature dependent viscosity. In this aspect of the invention it is preferred that the polymeric core incorporates neutralized ionizable monomers, which monomers are substantially hydrated.

The invention also provides an aqueous dispersion of water insoluble heteropolymer
30 particles, wherein said heteropolymer particles incorporate units of hydrophilic ionizable monomers and reactive amphiphile throughout the particles.

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The aqueous dispersions of the present invention may be used as a thickener or binder in a paint. In such application the dispersions are added to or combined with conventional paint additives or components to provide a paint base or composition of the required characteristics. Examples of suitable paint additives, in addition to the binder, include
5 thickeners, antifungal agents, UV absorbers, extenders, pigments etc. Some of these additives may be precombined with the aqueous dispersions before incorporation into the paint composition. The aqueous dispersions may also be used as binders or thickeners for adhesives, textile coatings, carpet backings and construction materials. In these applications the dispersions may be combined with additives and components known in the
10 art.

The aqueous dispersions of the present invention exhibit a temperature dependent viscosity which makes them useful in many applications in the coatings and adhesives industries.

15 Such dispersions are useful as self thickening sole binders for coatings. In this application the water swelling behaviour of the hydrophilic core material may be used to assist in film formation such that the conventional co-solvents normally used for this purpose are reduced or even eliminated. In addition to the environmental advantages, paints formulated in this way have a highly favourable cost/performance balance.

20

In a further embodiment of the invention, dispersions are formulated which show extremely high viscosity and even viscosity which increases with shear rate. Such dispersions can be blended with conventional paint making ingredients to give working paints with reduced levels of additive thickeners. The dispersions formulated in this way
25 are able to display their viscosity characteristics at lower levels of acid monomer than those formulated with conventional alkali swellable thickener technology.

In order to facilitate an understanding of the invention reference will be made to the accompanying examples which illustrate some preferred aspects of the invention.

30 However it is to be understood that the particularity of the following description is not to supersede the generality of the invention hereinbefore described.

EXAMPLES

In the examples the following abbreviations have the meanings indicated:

5 Glossary of Monomer abbreviations**MONOMER NAME**

	acrylamide	AAM
	acrylic acid	AA
	butyl acrylate	BA
10	tert-butyl acrylate	TBA
	tert-butylaminoethyl methacrylate	TBAEMA
	N,N-dimethylaminoethyl methacrylate	DMAEMA
	ethyl acrylate	EA
	glyceryl propoxy triacrylate	GPTA
15	triethylene glycol diacrylate	TEGDA
	Trimethylolpropane trimethacrylate	TMPTMA
	glycidyl methacrylate	GMA
	methacrylic acid	MAA
	methyl methacrylate	MMA
20	styrene	ST

Example 1**a) (ii) First monomer feed**

- 25 An aqueous emulsion of copolymeric particles was made by the following method:
 A first monomer emulsion was made by adding to a vessel, 86.8g of ethyl acrylate,
 119.1g of methyl methacrylate, 2.1g of glyceryl propoxy triacrylate (Sartomer
 SR9020) and 5.7g of acrylic acid. To this mixture 91g of an ethoxylate (12EO) of
 HD-Ocenol 110/130 (Henkel) with a cloud point of 74-78°C was added. To the
 30 monomer mixture was added 6.1g of a 30% solution of sodium dodecyl sulfate in
 water, and 522.7g of de-ionised water, and an emulsion formed under shear.

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(ii) Second monomer feed

A second monomer emulsion was made by mixing 35.3g of ethyl acrylate, 111.9g of methyl methacrylate, 2.8g of acrylic acid and 1.5g of glyceryl propoxy triacrylate. To the monomer mix was added 3.0g of a 30% solution of sodium dodecyl sulfate in water, and 267.6g of deionised water. An emulsion was formed under shear.

(iii) Initiator feed

A solution of initiator was made by mixing 96.38g of water, 1.93g of ammonium persulfate, and 0.34g of sodium carbonate.

(iv) Precursor stage

342.2g of deionised water and 3.6g of 30% sodium dodecyl sulfate in water were added to a round bottomed flask at 90°C, with stirring.

(v) Initiator spike

A mixture of 0.13g of ammonium persulfate, 0.95g of de-ionised water and 0.18g of sodium carbonate was added to the reaction flask.

(vi) Polymerisation

Ten minutes after the addition of the initiator spike, the first monomer feed and initiator feed were pumped into the reaction flask under stirring. The first monomer feed was added to the reaction vessel over a period of 160 minutes, followed by the second monomer feed over 80 minutes. The initiator feed was added over the full 240 minute period.

(vii) Dilution and Mop-up

After completion of the 240 minute period, 89.3g of water was added, followed by five consecutive initiator additions at 10 minute intervals, alternating between sodium sulfite formaldehyde (0.3g) in water (8.1g) and tertiary butyl

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hydroperoxide (0.5g) mixed with water (8.1g).

(viii) Post-addition

After a further 10 minutes, 7.2g of a 25% ammonium hydroxide solution was added with 11.6g of water. Subsequently, after 30 minutes, the latex was cooled to room temperature, and 0.1g of the defoamer Bevaloid 4226 (Rhone Poulenc) 0.9 g of Proxel GXL (Zeneca) and 161.6g of water added.

- b) (Comparative) The procedure was repeated, except an ethoxylate (40EO) of HD-Ocenol 110/130 (Henkel) having a cloud point greater than 100°C was used in place of the 12EO ethoxylate as the reactive amphiphile. The resulting latex was water thin (<20 rpm Brookfield viscosity, spindle 2, 20 rpm).
- c) (Comparative) The procedure was repeated, except an ethoxylate (20EO) of HD-Ocenol 110/130 having a cloud point greater than 100°C was used in place of the 12EO ethoxylate as the reactive amphiphile.

The solids content and viscosities of the dispersions of Examples 1 and 3 were measured. The results are shown in Table 1 below.

20

Table 1

Dispersion	Ocenol Ethoxylation	Solids (%nv)	Brookfield viscosity (cP) ¹	Cone & Plate viscosity (P)
1a	12EO	22.36	58,000	1.9
1c	20EO	22.55	132	0.28

¹Brookfield viscosity at 20 rpm

25

Example 2

The procedure of example 1 was repeated except 7-Octen-1-ol:1 butylene oxide:10 ethylene oxide having a cloud point of 75°C was used as the reactive amphiphile and the

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amount of water at each stage was reduced. The compositions of the various stages are shown in Table 2 below.

Table 2

5	Precursor stage	g
	de-ionised water	306.03
	30% sodium dodecyl sulfate	4.61
	Initiator feed	
10	Sodium carbonate	0.23
	de-ionised water	0.85
	ammonium persulfate	0.17
	Initiator spike	
15	de-ionised water	86.20
	ammonium persulfate	2.50
	sodium carbonate	0.44
	First monomer feed	
20	de-ionised water	467.48
	30% sodium dodecyl sulfate	7.83
	EA	112.96
	MMA	154.89
	GPTA (glyceryl propoxytriacylate)	2.76
25	AA	7.89
	7-octen-1-ol:1BO:10EO	118.34
	Sec nd monomer feed	

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	de-ionised water	241.62
	30% sodium dodecyl sulfate	3.91
	EA	45.86
	MMA	145.45
5	GPTA	1.97
	AA	3.94
	de-ionised water	72.64
10		
	Mop-up	
	de-ionised water	14.53
	sodium sulfite formaldehyde	0.34
15	de-ionised water	7.26
	tert-butyl hydroperoxide	0.70
	de-ionised water	7.26
	sodium sulfite formaldehyde	0.34
20		
	de-ionised water	7.26
	tert-butyl hydroperoxide	0.70
	de-ionised water	7.26
25	sodium sulfite formaldehyde	0.34
	Post-addition	
	de-ionised water	10.36

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ammonium hydroxide	9.29
Bevaloid 4226	0.14
de-ionised water	7.26
Proxel GXL	1.12
de-ionised water	137.25

10

The solid content and viscosity of the dispersion was measured before and after dilution of the latex and the results are shown in Table 3 below.

Table 3

15	% surfactant	solids	Brookfield viscosity (cP)¹	Rotothinner (P)	Cone and Plate viscosity
	22	26.11 ²	solid	solid	0
	22	diluted to 21.46	10,520	> 15	2.15

¹Brookfield viscosity at 20 rpm

²Formula solids 30%. Latex diluted to avoid solidification.

20

Example 3

- a) The procedure of Example 2 was repeated, except 7-octen-1-ol:7EO having a cloud point of 79°C was used as the reactive amphiphile.
- b) The procedure was repeated except 37% 7-octen-1-ol:14EO having a cloud point of 97-100°C was used as an approximate molar replacement of the 22% 7-octen-1-ol:7EO.

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The solids content and viscosities of the dispersions were measured. The results are shown below in Table 4.

Table 4

Dispersion	Non-ionic Surfactant	%nv	Gel Content (%)	Brookfield viscosity (cP) ¹	Cone/Plate viscosity (P)
3a	7-octen-1-ol:7EO	25.79	89	Solid	Solid
3b	7-octen-1-ol:14EO	24.38	41	40,550	0.625

Notes:

1. Measured at 20 rpm on spindle no. 2.

Although a large amount of 7-octen-1-ol:14EO was incorporated into the particles at the reaction temperature (below cloud point), cooling of the latex prompted little or no further uptake of water to swell the particles and cause further thickening.

Example 4

- a) The procedure of Example 1 was repeated, except the monomer composition was altered to include butyl acrylate instead of ethyl acrylate. The resulting monomer composition in the first monomer feed contained 146.9g of methyl methacrylate, 59.2g of butyl acrylate, 2.1g of glyceryl propoxy triacrylate and 5.7g of acrylic acid. The second monomer feed contained 123.1g of methyl methacrylate, 24.1g of butyl acrylate, 1.52g of glyceryl propoxy triacrylate and 2.83g of acrylic acid.
- b) (Comparative) The procedure was repeated, except the composition of the various stages was as shown in Table 5 below:

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Table 5

Precursor stage		g
5	de-ionised water	314.61
	30% sodium dodecyl sulfate	5.46
	Initiator feed	
	Sodium carbonate	0.27
10	de-ionised water	1.46
	ammonium persulfate	0.20
	Initiator spike	
	de-ionised water	114.25
15	ammonium persulfate	2.95
	sodium carbonate	0.52
	First monomer feed	
	de-ionised water	385.24
20	30% sodium dodecyl sulfate	9.27
	AA	8.92
	MMA	212.27
	GPTA (glyceryl propoxytriacylate)	3.11
	BA	86.09
25	Ocenol:12EO	153.00
	Second monomer feed	
	de-ionised water	159.51

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	30% sodium dodecyl sulfate	4.64
	AA	4.33
	MMA	188.23
	GPTA	2.32
5	BA	36.86
	de-ionised water	82.79
	Mop-up	
10	de-ionised water	16.56
	sodium sulfite formaldehyde	0.40
	de-ionised water	8.28
	tert-butyl hydroperoxide	0.83
15		
	de-ionised water	8.28
	sodium sulfite formaldehyde	0.40
	de-ionised water	8.28
20	tert-butyl hydroperoxide	0.83
	de-ionised water	8.28
	sodium sulfite formaldehyde	0.40
25	Post-addition	
	de-ionised water	11.81
	ammonium hydroxide	10.96

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	Bevaloid 4226	0.17
	De-ionised water	8.28
	Proxel GXL	1.32
5	de-ionised water	156.43

The solids content and viscosity of the dispersions were measured. The results are shown in Table 6 below.

10

Table 6

Dispersion	Solids (%nv)	BA content ¹	Brookfield viscosity (cP) ²	Cone & Plate viscosity (P)
4a	22.15	18.26	8	0.03
4b	29.46	17.69	> 100 000	4.2

15 ¹BA as a percentage of total latex solids.

²Brookfield viscosity at 20 rpm.

³MMA/BA/2% AA/20% Ocenol:12EO.

⁴MMA/BA/3% AA/22% Ocenol:12EO.

20 With MMA/BA rather than MMA/EA, higher solids may be required to achieve the desired thickening.

Example 5

25 a) The procedure of Example 1 was repeated except trimethylolpropane trimethacrylate was used as the crosslinking agent, rather than GPTA. The substitution was on a weight basis.

b) The procedure of Example 1 was repeated, except triethylene glycol diacrylate (TEGDA) was used as the crosslinking agent, rather than GPTA.

30

The viscosity of the dispersions was measured and compared to the viscosity of the dispersion obtained in Example 1a. The results are shown below in Table 7.

Table 7

Dispersion	Crosslinker	%nv	Gel Content ² (%)	Brookfield viscosity (cP) ¹	Cone/Plate viscosity
1a	GPTA	22.36	60	58,000 ¹	1.91
5a	TEGDA	22.42	60	9,150 ¹	1.76
5b	TMPTMA	22.60	50	Solid	Solid

¹ Measured at 2 rpm.

² % of polymer insoluble in THF under ATM 556.5.

Example 6

a) (i) First monomer feed

An aqueous emulsion of copolymeric particles was made by the following method:

A first monomer emulsion was made by adding to a vessel, 43.16g of ethyl acrylate, 59.19g of methyl methacrylate, 1.06g of glyceryl propoxy triacrylate (Sartomer SR9020) and 3.01g of acrylic acid. To this mixture 45.22 of an ethoxylate phosphate of HD-Ocenol 110/130 (Henkel). The surfactant was ethoxylated to approximately 10 moles. To the monomer mixture was added 3.0g of a 30% solution of sodium dodecyl sulfate in water, and 258.9g of de-ionised water, and an emulsion formed under shear.

(ii) Second monomer feed

A second monomer emulsion was made by mixing 17.53g of ethyl acrylate, 55.58g of methyl methacrylate, 0.75g of acrylic acid and 0.75g of glyceryl propoxy triacrylate. To the monomer mix was added 1.5g of a 30% solution of sodium dodecyl sulfate in water, and 133.8g of deionised water. An emulsion was formed under the shear.

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(iii) Initiator feed

A solution of initiator was made by mixing 47.74g of water, 0.95g of ammonium persulfate, and 0.17g of sodium carbonate

5 (iv) Precursor stage

342.2g of deionised water and 3.6g of 30% sodium dodecyl sulfate in water were mixed in a round bottomed flask at 90°C, with stirring.

(v) Initiator spike

10 A mixture of 0.06 of ammonium persulfate, 0.47g of deionised water and 0.09g of sodium carbonate were added to the reaction flask.

(vi) Polymerisation

15 Ten minutes after the addition of the initiator spike, the first monomer feed and initiation feed were pumped into the reaction flask under stirring. The first monomer feed was added to the reaction vessel over a period of 160 minutes, followed by the second monomer feed over 80 minutes. The initiator was added over the full 240 minute period.

20 (vii) Dilution and Mop-up

After completion of the 240 minute period, 40.23g of water was added, followed by five consecutive initiator additions at 10 minute intervals, alternating between sodium sulfite formaldehyde (0.13g) in water (4.0g) and tertiary butyl hydroperoxide (0.13g) mixed with water (4.0g).

25

(viii) Post-addition

After a further 10 minutes, 3.55g of a 25% ammonium hydroxide solution was added with 5.74g of water. Subsequently, after 30 minutes, the latex was cooled to room temperature, and 0.05g of Bevaloid 4226 (Rhône Poulenc), 0.4g of Proxel
30 GXL (Zeneca) and 76.1g of water added.

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- b) (Comparative) The procedure was repeated except Ocenol:3EO sulfate (no cloud point at pH of polymerisation) was used instead of Ocenol:10EO phosphate.
- c) (Comparative) The procedure was repeated except on a 2kg scale and the
 5 Ocenol:ethoxylate phosphate was included in the precursor stage (with the initial charge of water and sodium dodecyl sulfate in the reactor) rather than in the first monomer feed. In addition, 4.02g of sodium carbonate was added to the precursor stage.
- 10 d) (Comparative) The procedure was repeated, except ammonia was used to bias the pH to 9 rather than adding sodium carbonate.

The viscosities of the dispersions were then measured and the results are as shown in
 Table 8

15 below.

Table 8

Example	pH ¹	Surfactant	pH biasing agent	%nv	Gel Content (%)	Dw (nm)	Brookfield Viscosity ² (cP)	Cone/Plate viscosity (P)
6a	3	Ocenol:10EO phosphate	None	23.15	63	1690	1200	0.4
20 6a (pH raised after polymerisation)	10	Ocenol:10EO phosphate	None	---	---	---	---	1.2
6b	7	Ocenol:3EO phosphate	None	22.04	0	---	0	0.5
6c	7	Ocenol:10EO phosphate	Na ₂ CO ₃	22.90	5	79	40	0.14
25 6d	9	Ocenol:10EO phosphate	Ammonia	22.61	3	30	50	0.04

¹ of process

² Brookfield viscosity at 20 rpm.

Example 7**a) (i) First monomer feed**

5 An aqueous emulsion of copolymeric particles was made by the following method:
A first monomer emulsion was made by adding to a vessel, 94.8g of ethyl acrylate,
130.0g of methyl methacrylate, 2.32g of glyceryl propoxy triacrylate (Sartomer
SR9029) and 6.2g of acrylic acid. To this mixture 99.3g of an ethoxylate of HD-
10 Ocenol 110/130 (Henkel) with a cloud point of 74-78°C was added. To the
monomer mixture was added 10.0g of a 30% solution of sodium dodecyl sulfate in
water, and 570.5g of de-ionised water, and an emulsion formed under shear.

(ii) Second monomer feed

15 A second monomer emulsion was made by mixing 38.6g of ethyl acrylate, 122.0g of
methyl methacrylate, 3.1g of acrylic acid and 1.7g of glyceryl propoxy triacrylate.
To the monomer mix was added 5.0g of a 30% solution of sodium dodecyl sulfate in
water, and 196.6g of deionised water. An emulsion was formed under shear.

(iii) Initiator feed

20 A solution of initiator was made by mixing 105.2g of water, 2.1g of ammonium
persulfate, and 0.37g of sodium carbonate.

(iv) Precursor stage

25 373.5g of deionised water and 7.5g of 30% sodium dodecyl sulfate in water were
mixed in a round bottomed flask at 80°C, with stirring.

(v) Initiator spike

A mixture of 0.14g of ammonium persulfate, 1.0g of deionised water and 0.2g of
sodium carbonate were added to the reaction flask.

(vi) Polymerisation

Ten minutes after the addition of the initiator spike, the first monomer feed and initiator feed were pumped into the reaction flask under stirring. The first monomer feed was added to the reaction vessel over a period of 160 minutes, followed by the second monomer feed over 80 minutes. The initiator feed was added over the full 240 minute period.

(vii) Dilution and Mop-up

After completion of the 240 minute period, 59.1g of water was added, followed by three consecutive initiator additions at 10 minute intervals; sodium sulfite formaldehyde (0.14g) in water (11.82g), tertiary butyl hydroperoxide (0.30g) mixed with water 911.82g) and sodium sulfite formaldehyde (0.14g) in water (11.82g).

(viii) Post-addition

After a further 30 minutes, 7.8g of a 25% ammonium hydroxide solution was added with 8.4g of water. Subsequently, after 30 minutes, the latex was cooled to room temperature, and 0.1g of Bevaloid 4226 (Rhone Poulenc), 0.95g of Proxel GXL (Zeneca) and 117.6g of water added.

20 b) The procedure was repeated, except the polymerisation was conducted at 85°C.

c) The procedure was repeated, except the temperature of the polymerisation was 90°C.

The viscosities of the dispersions were measured. The results are shown in Table 9 below.

25

Table 9

Example	Solids (% nv)	Polymerisation Temperature (°C)	Gel Content (%)	Viscosity Bf¹ (cP)	Rotothinner Visc sity (P)	Cone & Plate Visc sity
7a	21.9	90	48	47 000	---	0.83

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Example	Solids (% nv)	Polymerisation Temperature (°C)	Gel Content (%)	Viscosity Bf ¹ (cP)	Rotothinner Viscosity (P)	Cloud Point & Plate Viscosity
7b	18.39	85	57	5 500	> 20	0.91
7c	22.38	80	73	5	0.1	0.1

¹Brookfield viscosity at 2 rpm.²Theoretical solids 25% nv.5 ³Theoretical solids 22.93% nv. Extra water was added to prevent solidification during cooling.

This comparison between different polymerisation temperatures demonstrates that the thickening process is temperature dependent. In order to obtain optimum thickening, the polymerisation temperature should be above the cloud point, in this case, 74-78°C.

10

Example 8**a) Aqueous dispersion**15 **(i) First monomer feed/monomer spike**

A first monomer emulsion was made by adding to a vessel, 59.46g of ethyl acrylate, 58.50g of methyl methacrylate, 3.54g of acrylic acid. 6.07g of this monomer mixture is put to one side to form the monomer spike. To the remaining mixture, 52.07g of an ethoxylate of HD-Ocenol 110/130 (Henkel) with a cloud point of 74-78°C was added. To the remaining monomer mixture was added 3.44g of a 30% solution of sodium dodecyl sulphate in water, and 262.49g of deionised water and an emulsion formed under shear.

20 **(ii) Second monomer feed**

A second monomer emulsion was made by mixing 199.00g of ethyl acrylate, 115.97g of methyl methacrylate, 6.57g of acrylic acid and 0.81g of glyceryl propoxy triacrylate. To the monomer mix was added 6.40g of a 30% solution of sodium dodecyl sulphate in water and 503.91g of deionised water. An emulsion was formed under shear.

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(iii) Initiator feed

A solution of initiator was made by mixing 92.19g of deionised water, 2.09g of ammonium persulphate, and 0.37g of sodium carbonate.

5 (iv) Precursor stage

319.41g of deionised water and 3.87g of 30% sodium dodecyl sulphate in water were mixed in a round bottomed flask at 90°C with stirring.

(v) Initiator spike

- 10 A mixture of 0.14g of ammonium persulphate, 8.77g of deionised water and 0.19g of sodium carbonate were added to the reaction flask.

(vi) Polymerisation

- The initiator spike was added to the precursor stage at 90°C and held for 5 minutes, followed
15 by the monomer spike and a further hold at temperature for 5 minutes. The first monomer feed was pumped to the reaction flask under stirring over a period of 160 minutes, followed by the second monomer feed over 80 minutes. The initiator feed was added over the full 240 minute period whilst maintaining the temperature between 89-90°C.

20 (vii) Dilution and Mop-up

- After completion of the 240 minute period, 77.69g of deionised water was added, followed by consecutive initiator additions at 10 minute intervals; sodium formaldehyde sulphonylate(0.28g) in deionised water(15.54g), tertiary butyl hydroperoxide(0.59g) mixed with deionised water(7.77g), sodium formaldehyde sulphonylate(0.28g) in deionised water(7.77g).
25 tertiary butyl hydroperoxide(0.59g) mixed with deionised water(7.77g), and finally sodium formaldehyde sulphonylate(0.28g) in deionised water(7.77g).

(viii) Post-addition

- After a further 30 minutes, 7.79g of a 25% ammonium hydroxide solution was added with
30 11.08g of deionised water. Subsequently, after 30 minutes, the latex was cooled to room temperature, and 0.12g of Bevaloid 4226(Rhone Poulenc), 0.94g of Proxel GXL (Zeneca) and

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154.56g of deionised water was added.

After cooling and testing the latex had the characteristics shown below in Table 10.

TABLE 10

5	Brookfield Viscosity (cP) spindle 2, 20rpm	Rotothinner Visco (P) @25°C	Cone & Plate (P) @25°C
	3,550	7.9	1.14

b) Paint formulation

10 Sealer/binder paints were prepared according to the following formulation.

	Material	Standard Paint	Test Paint
A	De-ionised water	101.20	101.20
	Dispersant	1.00	1.00
15	B		
	Dispersant	4.80	4.80
	Triton CF10	3.00	3.00
	Bevaloid 66811.001.00		
20	C		
	Titanium dioxide	190.00	190.00
	Silica Diafil 530	30.00	30.00
	Eckalite Clay	25.00	25.00
	D		
	Latex	310.00*	576.60**
25	De-ionised water	283.90	17.30
	Proxel 1.601.60		
	Thickener RM 1020 NPR	6.50	0.00
	E		
	Bevaloid 6681	1.00	1.00
30	F		
	Thickener RM 1020 NPR	41.00	0.00

* Commercial anionic acrylic latex 46.5% solids, Rohm & Haas Primal PR3230

** Latex is produced in Example 8a 25% solids

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The paint was produced by dispersing the C stage pigments into the combined A plus B stages. The finished millbase is added to the pre-mixed D stage in a separate vessel and adjusted with E and F stages.

5 The properties of the paints are shown below in Table 11.

Table 11

	Viscosity	Standard Paint	Test Paint
10	Brookfield cP	11,380	11,060
	Cone & Plate P	1.22	0.71
	Rotothinner P	6.7	4.5

15 When tested as a sealer/binder paint the test paint (having no coalescing aids or external thickeners) had equivalent or better performance compared to the standard paint.

Example 9

20 (i) Monomer emulsion stage

A monomer emulsion was prepared directly in a reaction vessel by adding the following components in order, 70.00g of methyl methacrylate, 70.00g of butyl acrylate, 0.20g of glyceryl propoxy triacrylate, 60.0g of an ethoxylate (9EO) of HD-Ocenol 110/130 (Henkel) with a cloud point of 57°C, 4.00g of Rhodapex CO436 (Rhodia) and 276.09g of deionised water. The

25 mixture heated to 80°C under a nitrogen atmosphere.

(ii) Initiator feed

A solution of initiator was made by mixing 2.00g of ammonium persulphate and 12.00 g of deionised water.

(iii) Initiator spike

Two separate solutions were made by mixing in the first, 0.26g of tertiary butyl perbenzoate and 2.66g of deionised water. The second spike solution was made by mixing 0.13g of sodium erthyorbate with 2.66g of deionised water.

5

(iv) Polymerisation

The initiator feed was added to the monomer emulsion stage at 80°C at the rate of 1ml/minute so as to control the level of reaction exotherm between 80-87°C. After 15 minutes add initiator spike stages and commence cooling.

10

(b) (Comparative) The procedure was repeated, except that and ethoxylate (12EO) of HD-Ocenol 110/130 having a cloud point of 99°C was used in place of the 9EO as the reactive amphiphile.

15 (c) (Comparative) The procedure was repeated, except that the reactive amphiphile was omitted from the monomer emulsion stage completely. The monomer emulsion stage was made by mixing 100.00g of methyl methacrylate, 100.00g of butyl acrylate, 0.20g of glyceryl propoxy triacrylate, 4.00g of Rhodapex C)436 (Rhodia) and 276.09g of deionised water.

20 The solids content were adjusted to match closely so that viscosities could be compared. The results are shown below in Table 12.

Table 12

Dispersion	Ocenol	Cloud Point °C	Solids %	Brookfield viscosity (cP)
25 1a	9EO	57	34.7	388
1b	12EO	99	36.5	64
1c	-	-	35.0	10

Those skilled in the art will appreciate that the invention described herein is susceptible to
 30 variations and modifications other than those specifically described. It is to be understood

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that the invention includes all such variations and modifications. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

5

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

10

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Orica Australia Pty Limited

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By DAVIES COLLISON CAVE
Patent Attorneys for the Applicant

